

(12) **UK Patent Application** (19) **GB** (11) **2 323 327** (13) **A**

(43) Date of A Publication **23.03.1998**

X

(21) Application No **9705510.7**

(22) Date of Filing **18.03.1997**

(71) Applicant(s)
Hoechst Trespaphan GmbH
(Incorporated in the Federal Republic of Germany)
Bergstrasse, D-66539 Neunkirchen,
Federal Republic of Germany

(72) Inventor(s)
Paul Malcolm Mackenzie Davidson
Rebecca Karen Govier
Helen Ann Biddiscombe
Marc Fritz Manfred Ott

(74) Agent and/or Address for Service
J A Claisse
John Claisse & Co, 97 Portway, WELLS, Somerset,
BA5 2BR, United Kingdom

(51) INT CL⁶
B32B 27/32

(52) UK CL (Edition P)
B5N N195 N196 N207 N21Y N212 N216 N223 N255
N259 N26X N260 N281 N262 N265 N266 N2708 N2730
N2732 N281 N283 N331 N353 N460 N469 N474 N478
N48X N491 N518 N519 N52Y N572 N584 N591 N603
N611 N62X N62Y N648 N650 N658 N661 N662 N663
N668 N672 N677 N680 N734 N735 N738 N759 N78X

(56) Documents Cited
None

(58) Field of Search
INT CL⁶ B32B 27/32
ONLINE:WPI

(54) Abstract Title
Polyolefin film

(57) A polyolefin film having a base layer of a polypropylene-based resin including microvoids formed by stretching a polypropylene-based resin containing the beta-form of polypropylene, and a heat seal layer on the base layer. When such films are heat sealed, the heat seal area becomes transparent, thereby providing an indication of seal integrity.

GB 2 323 327 A

Polymeric Films

This invention concerns polyolefin films produced from the beta-form of polypropylene.

The beta-form of polypropylene is relatively unstable compared with the corresponding alpha-form under the conditions usually used to produce polypropylene films. Thus when melts of polypropylene are extruded and then cooled to form a polymeric film, which may then subsequently be stretched, the alpha-form of polypropylene tends to predominate. However, it is known to produce films using polypropylene containing high concentrations of the beta-form of polypropylene by mixing polypropylene containing a high proportion of the alpha-form with a suitable nucleating agent which induces the formation of high concentrations of the beta-form when it is molten and subsequently cooled.

One example of such a process is described in US4386129 in which a variety of so-called beta-nucleators are dispersed in polypropylene following which films are produced therefrom by

melting and subsequent cooling, the crystallinity of the resulting cast films being controlled by appropriate adjustment of the cooling conditions. Selective extraction of the beta-form of the polypropylene from the films leaving a matrix of the alpha-form is then used to impart porosity to the films.

US5231126 describes the use of two component mixtures of beta-nucleating agents to produce microporous films by mono- or biaxial stretching cast polypropylene webs containing a high concentration of the beta-form of polypropylene resulting from the use of the mixture of nucleating agents. It is believed that the porosity results from voids induced by the change of the beta-form into the alpha-form during the stretching process, the alpha-form having a higher density than the beta-form from which it is derived. The development of porosity during the stretching process is accompanied by a significant reduction in apparent film density and the films become opaque with a high degree of whiteness.

More recently it has been proposed in EP0632095 to use a variety of organic amides as beta-nucleating agents in the formation of mono- and biaxially stretched polypropylene films, a melt of a mixture of polypropylene and the nucleating agent being cast into a film web which is allowed to crystallise at a temperature of 15 to 140°C to form a solid web containing the beta-form of polypropylene, following which the web is mono- or biaxially stretched at a temperature above 20°C but less than the melting point of the beta-form crystals in the web. The resulting stretched films are said to have high whiteness and hiding power combined with printability and writeability.

Microvoid formation during the plastic deformation of the beta-form of polypropylene is also described in the journal POLYMER (Vol. 35, No. 16, pp. 3442-5, 1995; and Vol.36, No.13, pp. 2523-30, 1995). Porosity is said to increase with higher crystallisation and lower stretching temperatures, all samples

containing the beta-form apparently becoming opaque when stretched at temperatures below 120-130°C.

Opacity due to microvoid formation also occurs when propylene homopolymers are blended with a variety of particulate materials and then biaxially stretched, numerous examples of this being known from the prior art. Typically, phase distinct organic or inorganic materials with a particle size of 1 to 10µm are used for the purpose.

According to the present invention there is provided a polyolefin film comprising a base layer of a polypropylene-based resin including microvoids formed by stretching a polypropylene-based resin containing the beta-form of polypropylene, and a heat seal layer on the base layer.

Films in accordance with the present invention will in general be heat sealable as a result of the presence of the heat seal layer, and they also have the advantage that when they are heat sealed the heat seal region can become optically clear compared with the rest of the film, thereby indicating whether the heat seal is properly formed. This is unlike heat sealable films which have been voided with particulates as the latter in general retain their opacity in the heat seal areas after heat sealing.

The polypropylene-based resin of the base layer is preferably formed from a propylene homopolymer or a random or propylene block copolymer containing a major proportion of units derived from propylene and having a crystallinity of greater than 40%.

The nucleating agent used to induce the formation of the beta-form of the polypropylene of the base layer can be selected from those proposed hitherto for the purpose. However, particularly good results have been achieved using amides as proposed in EP0632095, and more particularly N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide.

The amount of nucleating agent used to induce the formation of the beta-form of polypropylene can be varied, for example from 0.0001 to 5wt% of the nucleating agent based on the weight of polypropylene, as described in EP0632095, preferred amounts being from 0.001 to 1wt%.

The heat seal layer forms an outer surface of films of the present invention, and it can be in direct contact with the voided polypropylene base layer or it can be an outer layer on one or more intermediate layers on the base layer. The heat seal layer and any other layers which may be present are preferably formed from a polyolefin, examples of polymers which can be used for the purpose including polymers containing units derived from one or more of ethylene, propylene, butene-1 and higher aliphatic alpha-olefins, and blends thereof. Other polymeric materials which can be used for these layers include, for example, acrylic polymers, and polyolefins extended with unsaturated carboxylic acids and derivatives thereof, e.g. acid ionomers and anhydrides.

Although one surface of the voided base layer of films of the present invention will have a heat sealable layer thereon, the other surface of the base layer need not have any further layers thereon. This can be used, for example to exploit the often inherent printability of the base layer whilst providing films which are heat sealable. However, this other surface of the base layer can have one or more polymeric layers thereon, for example a further heat sealable layer which can be the same as or different from the heat seal layer on the other side of the base layer, preferred materials for this further heat seal layer being selected from heat seal materials which can be used for the heat seal layer on the other side of the voided polypropylene-based layer.

Films in accordance with the present invention can include one or more additives used in the polyolefin art, for example slip

agents, antistatic agents, antiblock agents, stabilizers, or UV absorbers or pigments, such additives preferably being present in amounts which do not significantly adversely affect the ability of polypropylene to crystallise in its beta-form. When additives are present, they can be in one or more of the layers of which the film is constructed. When a pigment is used, it is preferably present in an amount which does not substantially mask the change in opacity which results when the film are heat sealed.

Films in accordance with the present invention can be produced using known methods, for example by coextrusion through a slot die of melts of polymers of the two specified layers, or others which may be desired, for example intermediate layers, to form a polymer web which is cooled and thereafter sequentially biaxially stretched. However, the heat seal layer or layers can be applied to the voided layer by coating after the voided layer has been formed.

As will be appreciated from the prior art referred to above, it will generally be necessary to form the beta-form of the polypropylene-based resin in the base layer before the film is stretched to effect voiding, and this can be carried out by allowing a melt of the polypropylene-based resin and a beta-form nucleating agent to crystallise under conditions which bring about the formation of the beta-form of the resin. The cooling or crystallisation temperature used to induce the formation of the beta-form of the polypropylene resin of the base layer prior to stretching should be at least 20°C but less than the melting point of the beta-form of polypropylene. Although temperatures at the lower end of this range, for example up to 50°C, can be used, it is generally preferred to use temperatures of at least 70°C, and higher temperatures still are often preferred, for example 90°C or more. However, the cooling temperature is preferably not more than 140°C, and from practical considerations it is preferably below the temperature at which the film sticks to surfaces used to cool it.

Cooling of the melt can be effected in air of a suitable temperature, but it is generally preferred to effect cooling by contacting the extruded web with a cooling surface, for example a chill roll.

Subsequent biaxial stretching of the cooled web can be effected under conditions known in the polypropylene film art, the stretching preferably being effected sequentially, this enabling the conditions used in the two directions to be selected independently of each other. Stretching in the direction of extrusion (the machine direction) will usually be effected before stretching in the transverse direction.

The conditions used to effect stretching in the machine direction have been found to have a substantial effect on microvoid formation, lower stretch temperatures and lower stretch ratios usually leading to increased voiding. A preferred temperature range for stretching in the machine direction is from 70 to 110°C, and more preferably from 80 to 95°C, and the stretch ratio used in the machine direction will usually be at least 3:1, a preferred range being from 3.5:1 to 8:1.

Subsequent stretching of the films in the transverse direction will in general be effected at lower temperatures than are conventionally used for the transverse stretching of polypropylene films, for example at from 100 to 160°C. However, it is generally preferred to effect stretching in the transverse direction at temperatures of not more than 155°C and preferably not more than 150°C in order to produce biaxially stretched films having low densities. The stretch ratio used in the transverse direction is preferably from 3:1 to 10:1.

The heat seal layer of films in accordance with the present invention are preferably from 0.2 to 2.0µm thick, and preferably from 0.8 to 1.5µm thick. Films in accordance with the present

invention can in general be made to thicknesses used hitherto for heat sealable voided polypropylene films.

Either or both outer surfaces of films in accordance with the present invention are preferably treated to increase their surface energy, for example using flame and corona discharge treatment.

The following Examples are given by way of illustration only:-

Example 1

A two layer polymer web was produced by coextruding through a slot die a base layer of propylene homopolymer containing 0.1wt% of a beta-form nucleating agent (N,N'-dicyclo-hexyl-2,6-naphthalene dicarboxamide; NJ-Star NU-100, ex New Japan Chemical Co., Ltd.), and a single layer of a propylene/ethylene copolymer (4wt% ethylene). The homopolymer layer was cooled by bringing it into contact with a chill roll having a surface temperature of 100°C, and the copolymer layer was cooled in the ambient air.

DSC measurements indicated the homopolymer layer contained a high level of the beta-form of polypropylene with T_m of 153°C.

The cooled web was then stretched 4.5 times in the direction of extrusion by contacting them with heated rolls at 90°C and having different peripheral speeds to produce opaque mono-axially stretched web. DSC showed that virtually all of the beta-form of polypropylene formed during the cooling step had been converted into the alpha-form.

The mono-axially stretched web was then stretched 8.0:1 in the transverse direction using a stenter oven 144°C to produce biaxially stretched films with the density shown in Table 1. The thickness of the film produced is also shown in Table 1, the single heat seal layer being 1µm thick.

The copolymer layer had a heat seal threshold of 122°C, and an impulse heat seal formed between the copolymer layers was clear.

Example 2 (Comparison)

A single layer biaxially stretched and voided polypropylene film was produced in a similar manner to and under the conditions described in Example 1 except that the copolymer layer was omitted. This film did not form a heat seal to itself under the conditions used to form the heat seal described in Example 1.

Example 3 (Comparison)

A three layer polymer web was produced by coextruding a core layer of the propylene homopolymer used in Example 1 and 2 but containing chalk (mean particle size 3 μ m) as a voiding agent, with two outer layers of the copolymer used in Examples 1. The extruded web was cooled using a chill roller having a surface temperature of 20°C, and it was then stretched 4.5:1 in the machine direction using rolls heated at 110°C before being stretched 8:1 in the transverse direction in a stenter oven at a temperature of 160°C. The web could not be stretched in the transverse direction at the temperature used in Examples 1 and 2.

This film, which had heat seal layers which were both 1 μ m thick and had a heat seal threshold of 122°C, heat sealed to itself but the resulting heat seals were opaque.

Table 1

Example	Heat seal layer (yes/no)	TD Stretch Temp. (°C)	Total Thickness (µm)	Film Density (g/cm ³)	Heat seal Threshold (°C)/type
1	yes	144	54.0	0.59	122/clear
2	no	144	45.0	0.65	-/no seal
3	yes	160	50.0	0.75	122/opaque

Claims

1. A polyolefin film comprising a base layer of a polypropylene-based resin including microvoids formed by stretching a polypropylene-based resin containing the beta-form of polypropylene, and a heat seal layer on the base layer.
2. A polyolefin film according to claim 1, wherein the heat seal layer comprises a polymer containing units derived from at least two of ethylene, propylene, butene-1 or a higher alpha-olefin, a polyolefin extended with an unsaturated carboxylic acid or a salt or anhydride thereof, or an acrylic polymer.
3. A polyolefin film according to either of the preceding claims, wherein the surface of the base layer remote from the heat seal layer has a further polymeric layer thereon.
4. A polyolefin film according to claim 3, wherein the said further polymeric layer comprises a polymer as defined in claim 2 for the heat seal layer.
5. A polyolefin film according to any of the preceding claims, having an intermediate layer between the heat seal layer and the base layer.
6. A polyolefin film according to any of the preceding claims, wherein each layer thereof is substantially non-pigmented.
7. A polyolefin film according to any of the preceding claims, wherein the film has been biaxially stretched.
8. A polyolefin film according to any of the preceding claims, wherein formation of the beta-form of polypropylene used to form the voided base layer is induced using an appropriate nucleating agent.

9. A polyolefin film according to claim 8, wherein the nucleating agent comprises N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide.

10. A polyolefin film according to any of the preceding claims, which has been subjected to a treatment to increase its surface energy.

11. A film according to any of the preceding claims, wherein the layers thereof have been produced by coextrusion.

12. A film according to any of claims 1 to 10, wherein the heat seal layer has been applied by coating.

13. A film according to any of the preceding claims, wherein it contains a slip agent, an antistatic agent, an antiblock agent, a stabilizer, or a UV absorber.



The Patent Office

12.

Application No: GB 9705510.7
Claims searched: 1 to 13

Examiner: R.J.MIRAMS
Date of search: 9 June 1998

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.P):

Int CI (Ed.6): B32B 27/32

Other: ONLINE: WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	NONE	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.